Statistical and Thermal Physics: Final Exam

10 May 2016

Name: Taylor Larrechea **Total:** /60

Instructions

- There are 7 questions on 11 pages.
- Show your reasoning and calculations and always justify your answers.

Physical constants and useful formulae

$$R = 8.31\,\text{J/mol K} \qquad k = 1.38\times10^{-23}\,\text{J/K} \qquad N_A = 6.02\times10^{23}\,\text{mol}^{-1} \qquad 1\,\text{atm} = 1.01\times10^{5}\,\text{Pa}$$

$$N! \approx N^N e^{-N}\sqrt{2\pi N} \qquad \ln N! \approx N\ln N - N \qquad e^x \approx 1 + x \quad \text{if } x \ll 1$$

$$\int_{-\infty}^{\infty} e^{-ax^2}\mathrm{d}x = \sqrt{\frac{\pi}{a}} \qquad \int_0^{\infty} xe^{-ax^2}\mathrm{d}x = \frac{1}{2a} \qquad \int_0^{\infty} x^2e^{-ax^2}\mathrm{d}x = \sqrt{\frac{\pi}{4a^3}} \qquad \int_0^{\infty} x^3e^{-ax^2}\mathrm{d}x = \frac{1}{2a^2}$$

Question 1

A monoatomic ideal gas initially at temperature 200 K and with volume $2.0\times10^{-3}\,\text{m}^3$ and pressure $2.0\times10^{5}\,\text{Pa}$ is placed in contact with a bath at temperature 300 K. The pressure of the gas is held constant and the gas eventually reaches the same temperature as the bath (whose temperature remains constant).

a) Determine the work done and the heat absorbed by the gas.

$PV = NkT \;:\; \frac{P}{Nk} = \frac{T}{V} \;\therefore\; \frac{T_i}{V_i} = \frac{T_f}{V_f} \longrightarrow V_f = T_f \cdot \frac{V_i}{T_i}$

$V_f = \frac{300\,k}{200\,k} \cdot 2.0\times10^{-3}\,m^3 = \frac{3}{2}(2.0\times10^{-3}\,m^3) = 3.0\times10^{-3}\,m^3$

$W = -P\Delta V = -2.0\times10^5\,Pa(3.0\times10^{-3}\,m^3 - 2.0\times10^{-3}\,m^3) = -2.0\times10^5\,Pa(1.0\times10^{-3}\,m^3)$

$W = -200\,J$

$E = Q + W \;\therefore\; Q = E - W$

$Q = \frac{3}{2}P\Delta V + 200\,J = \frac{3}{2}(2.0\times10^5\,Pa)(1.0\times10^{-3}\,m^3) + 200\,J$

$Q = \frac{3}{2}(200\,J) + 200\,J$

$Q = 300\,J + 200\,J = 500\,J$

Question 1 continued ...

$$\boxed{W = -200\,J,\ Q = 500\,J}$$

b) Determine the change in entropy of the gas, the change in entropy of the bath and describe whether the second law is satisfied by the entire system.

$$\Delta S_{Gas} = C_p \int_{T_i}^{T_f} \frac{1}{T} dT = \frac{5}{2} Nk \cdot \ln(3/2) \quad : \quad Nk = \frac{PV}{T}$$

$$\Delta S_{Gas} = \frac{5}{2} \cdot \frac{2.0\times10^5 Pa(2.0\times10^{-3} m^3)}{200K} \ln(3/2) = 2.03\ J/K$$

$$\boxed{\Delta S_{Gas} = 2.03\ J/K}$$

$$\Delta S_B = \frac{Q}{T} = \frac{-500\,J}{300\,K} = -1.667\ J/K$$

$$\boxed{\Delta S_{Bath} = -1.67\ J/K}$$

$$\Delta S_{Tot} = 2.03\ J/K - 1.67\ J/K = 0.36\ J/K > 0$$

Yes 2nd law holds true

/15

Question 2

Answer either part a) or part b) for full credit for this problem.

a) The isobaric expansion coefficient for a system is

$$\alpha := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and the isothermal compressibility is

$$\kappa_T := -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Show that, for any system

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial P}{\partial T}\right)_V .$$

$$\frac{\alpha}{\kappa_T} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \cdot -V\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z \quad : \quad -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

$z = P$, $y = T$, $x = V$ $\therefore$

$$\boxed{-\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}} \quad \checkmark$$

Question 2 continued ...

b) Starting with the fundamental thermodynamic identity, obtain an expression for $\mathrm{d}H$ and

$$c_P = \left(\frac{\partial H}{\partial T}\right)_{P,N}$$

use the result to show that

$$c_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}.$$

$$dE = Tds - Pdv \quad , \quad H = E + PV$$

$$dH = dE + Pdv + vdP = Tds - \cancel{Pdv} + \cancel{Pdv} + vdP = Tds + vdP$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_{P,N} dT + \left(\frac{\partial s}{\partial P}\right)_{T,N} dP$$

$$dH = T\left(\frac{\partial s}{\partial T}\right)_{P,N} dT + \left(T\left(\frac{\partial s}{\partial P}\right)_{T,N} + v\right) dP \ : \ dH = \left(\frac{\partial H}{\partial T}\right)_{P,N} dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,N} dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP = T\left(\frac{\partial s}{\partial T}\right)_{P,N} dT + \left(T\left(\frac{\partial s}{\partial P}\right)_{T,N} + v\right) dP$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial s}{\partial T}\right)_{P,N} \quad \text{w/} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_{P,N}$$

$$\boxed{C_p = T\left(\frac{\partial s}{\partial T}\right)_{P,N}}$$

/6

Question 3

The entropy of a system is given by

$$S = S(E, V, N) = \frac{3}{2} Nk \ln\left(E + \frac{N^2 a}{V}\right) + Nk \ln (V - Nb).$$

a) Determine the energy equation of state $E = E(T, V, N)$.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N : \left(\frac{\partial S}{\partial E}\right)_N = \frac{3}{2} Nk \cdot \frac{1}{E + \frac{N^2 a}{V}}$$

$$\frac{1}{T} = \frac{3}{2} Nk \cdot \frac{1}{E + \frac{N^2 a}{V}} \to \frac{2}{3} \frac{1}{NkT} = \frac{1}{E + \frac{N^2 a}{V}}$$

$$E + \frac{N^2 a}{V} = \frac{3}{2} NkT \quad \therefore \quad \boxed{E = \frac{3}{2} NkT - \frac{N^2 a}{V}}$$

b) Describe *how* one can determine the pressure equation of state $P = P(T, V, N)$ for this system.

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_N : \left(\frac{\partial S}{\partial V}\right)_N = Nk \cdot \frac{1}{V - Nb} \quad \therefore \quad \frac{P}{T} = \frac{Nk}{V - Nb}$$

$$\boxed{P = \frac{NkT}{V - Nb}}$$

/6

Question 4

An isolated system consists of four distinguishable spin-1/2 particles, labeled A, B, C, D in a uniform magnetic field. The single particle pin up state, $\uparrow$, has energy $-\mu B$ and the spin down state, $\downarrow$, has energy $+\mu B$. Consider the following states:

	Particle A	Particle B	Particle C	Particle D	
State 1	$\uparrow$	$\uparrow$	$\downarrow$	$\downarrow$	$E=0$
State 2	$\downarrow$	$\uparrow$	$\downarrow$	$\uparrow$	$E=0$
State 3	$\downarrow$	$\downarrow$	$\downarrow$	$\uparrow$	$E=2\mu B$

Which of the following is true regarding the probabilty with which these states occur?

i) They are all equally probable.
ii) The probabilities are different for all three states.
iii) The probabilities for states 1 and 2 are the same, but different to that of state 3.
iv) The probabilities for states 2 and 3 are the same, but different to that of state 1.
v) The probabilities for states 1 and 3 are the same, but different to that of state 2.

/3

Question 5

Consider an Einstein solid with N particles and for which the number of energy units q satisfies $1 \ll q \ll N$. The multiplicity for this system is

$$\Omega \approx \left(\frac{eN}{q}\right)^q \frac{1}{\sqrt{2\pi q}}.$$

a) Show that the entropy is

$$S \approx kq\left[\ln\left(\frac{N}{q}\right) + 1\right].$$

negligible

$$S = k\ln[\Omega] = k\ln\left[\left(\frac{eN}{q}\right)^q \cdot \frac{1}{\sqrt{2\pi q}}\right] = k\left[\ln\left(\left(\frac{eN}{q}\right)^q\right) + \cancel{\ln\left(\frac{1}{\sqrt{2\pi q}}\right)}\right]$$

$$S = k\cdot\left[q\ln\left(\frac{eN}{q}\right) - \ln\left(\sqrt{2\pi q}\right)\right] = k\left[q\left(\ln(N/q) + \ln(e)\right)\right]$$

$$S = kq\left[\ln(N/q) + 1\right]$$

$$\boxed{S \approx kq\left[\ln(N/q) + 1\right]}$$

Question 5 continued ...

b) Note that the energy is $E = \hbar\omega\,(q + N/2)$. Determine the temperature in terms of energy.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N \quad : \quad \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial q}\right)\left(\frac{\partial q}{\partial E}\right) \quad : \quad \frac{E}{\hbar\omega} - \frac{N}{2} = q \quad : \quad \frac{2E - N\hbar\omega}{2\hbar\omega}$$

$$S = kq\left(\ln(N/q) + 1\right) = kq\ln(N/q) + kq$$

$$\frac{\partial S}{\partial q} = k\ln\left(\frac{N}{q}\right) + \cancel{kq}\,\frac{-1}{q} + \cancel{k} = k\ln\left(\frac{N}{q}\right), \quad \frac{\partial q}{\partial E} = \frac{1}{\hbar\omega}$$

$$\frac{1}{T} = \frac{k}{\hbar\omega}\ln\left(\frac{N}{q}\right) = \frac{k}{\hbar\omega}\ln\left(\frac{2\hbar\omega q}{2E - N\hbar\omega}\right) \quad \therefore$$

$$\boxed{T = \frac{\hbar\omega}{k}\cdot\frac{1}{\ln\left(\frac{2\hbar\omega q}{2E - N\hbar\omega}\right)}}$$

/12

Question 6

A particular type of particle can be in one three states; these have energy $-\epsilon, 0, \epsilon$.

a) Consider two such particles which are distinguishable and which are in equilibrium with a bath at temperature T. List all possible states of the system of the two particles and show that the partition function of the system is

$$\cancel{Z = 2\left[1 + \cosh(\epsilon\beta) + \cosh(2\epsilon\beta)\right]}$$

$$Z = 3 + 4\cosh(\epsilon\beta) + 2\cosh(2\epsilon\beta)$$

where $\beta = 1/kT$.

$$e^{-\epsilon\beta},\ 1,\ e^{\epsilon\beta} \quad : \quad Z = \sum e^{-E_s\beta}$$

$$Z = 1 + e^{-\epsilon\beta} + e^{\epsilon\beta} \quad : \quad Z_{Ensemble} = Z_{single}{}^{N}$$

$$Z_S{}^{N} = (1 + e^{-\epsilon\beta} + e^{\epsilon\beta})(1 + e^{-\epsilon\beta} + e^{\epsilon\beta})$$

$$= 1 + e^{-\epsilon\beta} + e^{\epsilon\beta} + e^{-\epsilon\beta} + e^{-2\epsilon\beta} + 1 + e^{\epsilon\beta} + 1 + e^{2\epsilon\beta}$$

$$= 3 + 2e^{-\epsilon\beta} + 2e^{\epsilon\beta} + e^{-2\epsilon\beta} + e^{2\epsilon\beta}$$

$$2(e^{-\epsilon\beta} + e^{\epsilon\beta}) = 4\cosh(\epsilon\beta) \quad : \quad e^{-2\epsilon\beta} + e^{2\epsilon\beta} = 2\cosh(2\epsilon\beta)$$

$$\therefore \quad \boxed{Z = 3 + 4\cosh(\epsilon\beta) + 2\cosh(2\epsilon\beta)}$$

b) Determine the mean energy of the system.

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln(Z) \quad : \quad \frac{\partial}{\partial\beta}\ln\left(3 + 4\cosh(\epsilon\beta) + 2\cosh(2\epsilon\beta)\right)$$

$$\frac{\partial}{\partial\beta}\ln(Z) = \frac{4\epsilon\sinh(\epsilon\beta) + 4\epsilon\sinh(2\epsilon\beta)}{3 + 4\cosh(\epsilon\beta) + 2\cosh(2\epsilon\beta)}$$

$$\boxed{\bar{E} = \frac{-4\epsilon\sinh(\epsilon\beta) - 4\epsilon\sin(2\epsilon\beta)}{3 + 4\cosh(\epsilon\beta) + 2\cosh(2\epsilon\beta)}}$$

Question 6 continued . . .

c) Suppose that the two particles are indistinguishable Fermions. Determine the partition function of the system and the mean energy of the system.

$1, e^{-\epsilon\beta}, e^{\epsilon\beta} \quad \therefore \quad Z = 1 + e^{-\epsilon\beta} + e^{\epsilon\beta} = 1 + 2\cosh(\epsilon\beta)$

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln(Z) = -\frac{\partial}{\partial\beta}\ln(1+2\cosh(\epsilon\beta))$$

$$\bar{E} = -\frac{(2\epsilon\sinh(\epsilon\beta))}{1+2\cosh(\epsilon\beta)}$$

$$\boxed{\bar{E} = -\frac{2\epsilon\sinh(\epsilon\beta)}{1+2\cosh(\epsilon\beta)}}$$

/12

Question 7

Answer either part a) or part b) for full credit for this problem.

a) A free classical particle has energy $E = (p_x^2 + p_y^2 + p_z^2)/2m$. Consider an ensemble of N such distinguishable particles. Determine the partition function, the mean energy and the heat capacity for this system.

$$Z_{Ensemble} = Z_{single}^{N} \quad : \quad Z_{single} = \alpha \int e^{-(p_x^2+p_y^2+p_z^2)\beta/2m} \, dp_x dp_y dp_z$$

$$Z = \alpha \int e^{-p_x^2\beta/2m} dp_x \int e^{-p_y^2\beta/2m} dp_y \int e^{-p_z^2\beta/2m} dp_z \qquad \int_{-\infty}^{\infty} e^{-ax^2} \mathrm{d}x = \sqrt{\frac{\pi}{a}}$$

$$Z = \alpha \sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2m\pi}{\beta}} = \alpha \left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$\boxed{Z_{ENS} = \left(\alpha \left(\frac{2\pi m}{\beta}\right)^{3/2}\right)^{N}}$$

$$\bar{E} = \frac{-\partial}{\partial\beta} N \ln\left(\alpha\left(\frac{2\pi m}{\beta}\right)^{3/2}\right) = \frac{3N}{2}\cdot\frac{1}{\beta} = \frac{3}{2}NkT$$

$$\boxed{\bar{E} = \frac{3}{2}NkT}$$

$$C = \frac{\partial \bar{E}}{\partial T} = \frac{3}{2}Nk$$

$$\boxed{C = \frac{3}{2}Nk}$$

Question 7 continued . . .

b) Consider classical free particles at temperature T. Using the Maxwell speed distribution, determine the most likely speed for a single particle. By what factor will the temperature have to change to double the most likely speed?

$$P_{speed}(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-v^2 m/2kT} = \alpha v^2 e^{-v^2\gamma}$$

$$\frac{\partial P_s}{\partial v} = 0 : \quad \frac{\partial P_s}{\partial v} = 2\alpha v e^{-v^2\gamma} - 2\alpha\gamma v^3 e^{-v^2\gamma}$$

$$2\alpha v e^{-v^2\gamma} - 2\alpha\gamma v^3 e^{-v^2\gamma} = 0 \quad : \quad \cancel{2\alpha v e^{-v^2\gamma}} = \cancel{2\alpha}\gamma v^{\cancel{3}\,2} \cancel{e^{-v^2\gamma}}$$

$$1 = \gamma v^2 \quad \therefore \quad v^2 = \frac{1}{\gamma} \quad : \quad v^2 = \frac{2kT}{m} \quad \therefore \quad V_{mp} = \sqrt{\frac{2kT}{m}}$$

$$\boxed{V_{mp} = \sqrt{\frac{2kT}{m}}}$$

Temperature has to increase by a factor of 4.

/6